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Reactivity at dislocations in bismuth. Part 1.etchants containing trifluoroacetic acid and trichloroacetic acid

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There are quite a few papers in the literature that show the delineation of dislocations in bismuth single crystals (Lovell and Wernick 1959, Popkova and Predvoditelev 1970, Frawley and Childs 1970). There does not seem to exist any extensive study on the effect of the chemical composition of the etchant on the reactivity at dislocations in bismuth but for a few (Vaghari and Shah 1974, Joshi and Shah 1984, Maniar and Shah 1983). The present communication is an attempt in this direction.

Single crystals of bismuth were grown by the horizontal zone-levelling method. Metal of 5N purity, obtained from Nuclear Fuels Complex, Hyderabad, was used. Single crystals were cleaved in the conventional manner at liquid nitrogen temperature and optically smooth surfaces were used in the present investigation. The etchants were made from analytical grade reagents. The etchants were tested for revealing dislocations (Amelinckx 1964). The activation energies were found from plots of the logarithm of etch-pit width versus the reciprocal of the absolute temperature. Figures 1 and 2 are the plots of log W versus $1/T$ in etchants containing trifluoroacetic acid and trichloroacetic acid respectively. Table 1 gives the values of the activation energies for the lateral motion of steps at dislocations. The activation energy increases from 0.24 ± 0.01 eV to 0.38 ± 0.01 eV.

Etching the (111) cleavages of bismuth single crystals in etchants, made up of 2 cc fuming nitric acid to which 3 cc of 1N trifluoroacetic acid or trichloroacetic acid was added, for 5 seconds produced well defined, crystallographically aligned, triangular etch-pits at sites of dislocations of the type (111) [10$\bar{1}$]. Etching was performed from room temperature to 65°C. The etch-pit width was measured using a filar eye-piece.

The activation energy was calculated using the Arrhenius law

$$W = A \exp(-E/RT) \qquad (1)$$

where '*W*' is the etch-pit width, '*T*' the absolute temperature and '*A*' a constant. It was assumed that '*A*' and '*E*' donot change with temperature. The second

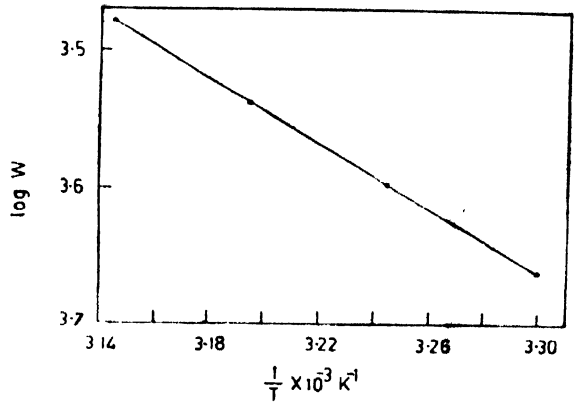

Figure 1. Plot of log *W* against $1/T$ for trifluoroacetic acid containing etchant.

term in eqn. (1) is more important, as it gives information of the reaction rates. Since '*E*' is always positive and a negative sign preceeds this term, the value of

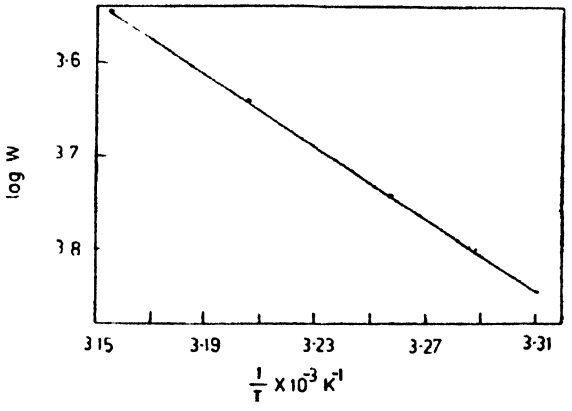

Figure 2. Plot of log *W* versus $1/T$ for trichloroacetic acid containing etchant.

'*E*' increases as the value of '*W*' decreases and hence the rate of the corresponding reaction.

Table 1. Etchant composition and activation energies.

	Etchant composition	Activation energy
1.	2 cc Fuming HNO_3 + 3 cc 1N CF_3COOH	0.24 ± 0.01
2.	2 cc Fuming HNO_3 + 3 cc 1N CCl_3COOH	0.38 ± 0.01

The formation of an etch-pit is a kinetic phenomena immediately following the nucleation of an appropriate 'hole'. There are two aspects of the kinetics,

namely, the nucleation of monomolecular steps at dislocations and the motion of steps away from the source (Gilman et *al* 1958, Cabrera 1960).

The situation regarding the role of dislocations in the attack of metal or alloy surfaces by corrosive fluids is confused. Three factors are said to govern the enhanced reactivity at dislocations ; namely, the extra energy at dislocations ; abnormal stereochemistry at dislocation cores and catalytic impurities which accumulate at dislocations (Thomas 1969).

The activation energy can be thought of as a barrier to the occurrence of the reaction. The greater the activation energy, slower the reaction rate. In this study addition of trichloroacetic acid in place of trifluoroacetic acid in the etchant causes an increase in the activation energy from 0.24 $\pm$ 0.01 eV to 0.38 $\pm$ 0.01 eV. It is conjectured that the change in the ionic size of the substituents retards the lateral motion of steps at dislocations. Further work is now under progress and will be reported in the next part.

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